peratures phonon-assisted transitions can occur to $\mathbf{k}\neq 0$ states lying well below the optical $\mathbf{k}=0$ levels of the 2500-Å transition.

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Rydberg States of Diatomic and Polyatomic Molecules Using Model Potentials

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We have used a simple model potential to calculate Rydberg series in N_2, O_2, CO, NO, ethylene, and benzene. The model potential for a molecule is taken as the sum of atomic potentials, which are calibrated to atomic data and contain no further parameters. Our results agree with experimentally measured values to within 5%–10% in all cases. We apply our results to several unresolved problems connected with the above molecules and indicate some of the applications which we foresee for model calculations.

I. INTRODUCTION

Recently, the pseudopotential method has become increasingly popular as a method for obtaining approximate descriptions of atomic and molecular Rydberg states.[1] In particular, Hazi and Rice[2] have given a successful treatment of some Rydberg states of the hydrogen, nitrogen, and benzene molecules using a simple and physically appealing model potential. Conceptually we can think of using a pseudopotential formalism to satisfy any orthogonality conditions between the Rydberg orbital and the core functions. To do this one replaces the orthogonality constraints in the eigenvalue equation by adding a nonlocal pseudopotential to the single-particle Hamiltonian without changing the Rydberg orbital eigenvalue.[1] The formal pseudopotential equations can be just as difficult to solve exactly as the original equations. But, as stressed by Hazi and Rice,[2] it is possible to use simple model potentials to reproduce many advantages of the exact pseudopotential formalism. These model potentials simplify the computations considerably and, in fact, since they are calibrated to experimental data, include effects not considered in the formal theory.[1]

In this paper we use model potentials to study the Rydberg states of the diatomic molecules O_2, N_2, CO, NO, and the polyatomic molecules ethylene and benzene. We assume that the effective potential of the molecular core can be represented by a sum of model potentials of the constituent atoms. However, the parameters of the model potential for each atom are determined by fitting its Rydberg spectrum to its experimental term values. The model potential for the molecule, expressed as a sum of these atomic potentials, contains no adjustable parameters. We then expand the Rydberg molecular orbital in terms of Gaussian-type orbitals located on each atomic center. The use of these basis functions provide both speed and flexibility for practical calculations on large polyatomic molecules. Most of the calculations reported in this paper can be done in a few minutes on a computer. The results are quite accurate, usually within 5% or 10% of available experimental results. It is not our intention to develop a scheme of high accuracy but simply to illustrate that the use of model potentials can provide results of comparable accuracy to those of more tedious and elaborate approaches. It is obvious that a direct SCF calculation of Rydberg states of large polyatomic molecules is presently not feasible and would probably not be worthwhile in any event.

These results on molecular Rydberg states are useful in studying the valence excited states of the same symmetry in many polyatomic molecules. Rydberg states can be quite close to and even on top of valence-shell transitions. Experimentally, such situations can usually be identified but ambiguities can arise in correlating the Hartree–Fock excited state spectra with the observed transitions. For example, our calculations show a Rydberg state in ethylene at 1.52 eV below the energy of $C_2H_4^+$ and therefore at 9.0 eV above the ground state.[3] This state is of the same symmetry as the

V state of the $N \rightarrow V$ transition ($\pi \rightarrow \pi^*$) observed at 7.6 eV above the ground state. We now ask where do these states lie in the Hartree–Fock approximation? The Rydberg (π, π^*) state must be at approximately 1.52 eV below the HF energy of $C_2H_4^+$. But direct SCF calculations give a Hartree–Fock ionization potential of 9.05 eV putting this Rydberg state of the same symmetry as the V state at 7.53 eV above the ground state in the Hartree–Fock approximation.[4] In fact, in the Hartree–Fock approximation the lowest state of (π, π^*) symmetry is a Rydberg state whereas spectroscopically the lowest state of this symmetry is the strong valence-shell transition at 7.6 eV with an oscillator strength of 0.34.

In Sec. II we begin with a discussion of the use of model and pseudopotentials in studying molecular Rydberg states. In Sec. III we describe in detail the procedure for obtaining the parameters for the atomic model potential from spectroscopic tables. Section IV is devoted to the related Rydberg spectra of the diatomics N_2, NO, O_2, and CO and Sec. V discusses the Rydberg spectrum of ethylene and its relation to valence excited states. Finally, in Sec. V we also calculate the various Rydberg states of benzene and use these results to interpret the electron impact spectrum of that molecule.

II. THEORY

In a Rydberg transition an electron is excited to an orbital large in size relative to a singly charged core. Moreover, the energy levels of these states can be expressed as

$$E_n = \text{I.P.} - R/(n-\delta)^2, \tag{1}$$

where I.P. is the ionization potential, R is the Rydberg constant, and δ is the quantum defect which may vary slightly with n. From Eq. (1) we know that Rydberg states are essentially hydrogenic in character which implies that the molecular core produces the potential of a monopole. The quantum defect δ measures the departure from this simple hydrogenic model and correlates with how the nodes and loops of the Rydberg orbital are displaced relative to analogous hydrogenic nodes and loops. With these properties it is obvious how one should apply a pseudopotential formalism to study Rydberg states. In an independent particle approximation the Rydberg orbital, ψ_R, must be orthogonal to the core solutions of the one-electron Hamiltonian, H, i.e.,

$$H\psi_R = \epsilon_R \psi_R, \tag{2a}$$

$$H\psi_c = \epsilon_c \psi_c, \tag{2b}$$

$$\langle \psi_R, \psi_c \rangle = 0. \tag{2c}$$

In pseudopotential theory one can replace the orthogonality constraints Eq. (2c), on the eigenvalue equation, Eq. (2a), by adding a pseudopotential V_S to H and solving the new eigenvalue equation[5]

$$(H + V_S)\phi_R = \epsilon_R \phi_R, \tag{3}$$

where ϕ_R is not subject to orthgonality constraints but the eigenvalue, ϵ_R, is unchanged. The Phillips and Kleinman V_S is the nonlocal operator

$$V_S = \sum_{\text{core}} (\epsilon_R - \epsilon_c) \, | \, \phi_c \rangle \langle \phi_c \, | . \tag{4}$$

Equation (3) with V_S of Eq. (4) is probably no simpler to solve at a practical level than is Eq. (2a) with its constraints Eq. (2c). However, as stressed in Ref. 2, we can construct much simpler model potentials which reproduce the main characteristics of the formal pseudopotential. Model potentials are flexible and usually contain some adjustable parameters. The resulting equations for the eigenvalues are much simpler than those of Eq. (3). To account for Eq. (1) the model potential must go as $-1/r$ at large r. The potential must have the symmetry of molecular framework and also account for penetration and exclusion effects.

For atomic Rydberg states one could use the model potential suggested by Abarenkov and Heine[6]

$$\begin{aligned} V_M &= A, && r < r_0, \\ &= \delta Z/r, && r \geq r_0, \end{aligned} \tag{5}$$

where δZ is the effective charge of the atom. This potential is constant inside a sphere of radius r_0 and Coulombic outside of the sphere. The model potential is an approximate representation of the effective potential $V + V_S$ where V is the single-particle potential in the Hamiltonian H of Eq. (2a). For a resonable choice of r_0 we can use V_M of Eq. (5) to solve for the atomic term values as a function of the parameter A. Comparison of the predicted term values with the experimental spectrum gives a unique choice for A. The only absolute requirement on a pseudo- or model potential is that it reproduces the eigenvalues of the real potential. Clearly V_M of Eq. (5) is not a correct representation of the true $V + V_S$ at all points in space. Outside the core it is probably a good representation of the effective potential but certainly it does not represent any meaningful potential inside the core. The true effective potential must have a complicated form inside the core which we really do not need to know. For practical purposes a simple model potential such as Eq. (5) imposes the proper boundary conditions and can therefore reproduce the eigenvalue spectrum. For further discussion including a justification for choosing V_M of Eq. (5) as an atomic model potential see Ref. 1.

For molecular applications we want a model potential with no additional adjustable parameters. To apply this model potential, Eq. (5), to molecular Rydberg states we assume that the molecular model potential is a simple superposition of the atomic potentials. All parameters of the atomic V_M are fixed by calibration to atomic term values for each atom separately. Hence,

$$V_{\text{mol}} = \sum_{\text{atoms}} V_{\text{atom}}. \tag{6}$$

We have found that including a term in Eq. (6) to

represent the hydrogen atom contribution has only a small effect on the eigenvalue spectrum. We will discuss this when we consider the ethylene spectrum, The results of the molecular calculation are also insensitve to the exact value of the atomic parameters.

We use Gaussian basis functions on the atomic and other centers to provide speed and flexibility in the numerical solution of the one-electron molecular problem. Although one has to use many such functions due to their incorrect asymptotic form, we feel that their other properties, especially the ease of computation with high n values and their general diffuseness outweigh other considerations. For the molecular calculations we used a computer program adapted from one provided by Winter. It utilizes only S, P_x, P_y, and P_z basis functions, but by placing these functions at other than atomic centers we can calculate molecular Rydberg states of various symmetries.

III. ATOMIC CALIBRATION

The solution of the one-electron Schrödinger equation for an atomic Rydberg state with V_M of Eq. (5), i.e.,

$$(-\tfrac{1}{2}\nabla^2+V_{\text{atom}})\psi_a{}^n=\epsilon_a{}^n\psi_a{}^n, \tag{7}$$

is easy. Writing

$$\psi_a{}^n=[r^{-1}R_{nl}(r)]Y_{lm}(\theta,\phi), \tag{8}$$

we have

$$(d^2R_{nl}/dr^2)+\{b-[l(l+1)/r^2]\}R_{nl}=0, \qquad r<r_0, \tag{9}$$

and

$$(d^2R_{nl}/dr^2)+\{a+(2/r)-[l(l+1)/r^2]\}R_{nl}=0, \qquad r\geq r_0, \tag{10}$$

where

$$b=2(\epsilon_a{}^n-A), \tag{11a}$$

$$a=2\epsilon_a{}^n. \tag{11b}$$

Solutions of Eq. (9) which vanish at $r=0$, are simple polynomials in $\sin b^{1/2}r$, $\cos b^{1/2}r$, and $b^{-1/2}r$ for $b>0$, similar polynomials in $\sinh|b|^{1/2}r$, $\cosh|b|^{1/2}r$, and $|b|^{-1/2}r$ for $b<0$, and r^{l+1} for $\epsilon_a{}^n=A$. We denote the solution of Eq. (9) for a given A by $\eta_A{}^l(\epsilon_a,r)$.

Solutions of Eq. (10) are just the Coulomb functions which decay exponentially at large r

$$\chi^l(r)={}^0U^l(r)+\gamma(N,l){}^1U^l(r) \tag{12}$$

with $N=1/|a|^{1/2}$ and

$$\gamma(N,l)=[N^{2l+1}\Gamma(N-l)\tan(N-l-1)\pi]/\Gamma(N+l+1). \tag{13}$$

The functions ${}^0U_l$ and ${}^1U_l$ are regular and irregular, respectively, at $r=0$ and are tabulated for $l=0$, 1, 2; $-1.2\leq a\leq-0.07$, $2.0\leq r\leq 15$ by Blume *et al.*[7] They[7] also tabulate the functions

$${}^0D^l=r(d/dr){}^0U^l, \qquad {}^1D^l=r(d/dr){}^1U^l \tag{14}$$

TABLE I. Core parameters from different atomic calibrations.[a]

	Singlet[b]	Triplet
Carbon	0.375	0.205
	Doublet	Quartet
Nitrogen	0.115	0.010
	Triplet	Quintet
Oxygen	0.045	−0.035

[a] Core parameters A of Eq. (5) (in atomic units).
[b] These headings specify the multiplicity of the Rydberg states used in the atomic calibration.

over the same range. We require the logarithmic derivatives $(d/dr)\ln\eta_A{}^l(\epsilon_A,r)$ and $(d/dr)\ln\chi^l(\epsilon_A,r)$ to be equal at the boundary $r=r_0$. The intersection of these plots determine the values of a for which a solution R_{nl} exists. In calibrating the atomic model potential we choose a series of A's and compare the eigenvalue spectrum with the experimental term values. We choose the parameter A which gives the best fit with experiment. Ideally A should be a function of l but we find that in practice we need to consider only $l=0$ in Eqs. (9) and (10). Consequently we calibrate only to the atomic ns series.

In determining the parameters for carbon, nitrogen, and oxygen, we may choose A to give agreement with either the atomic singlet or triplet levels for carbon, doublet or quartet for nitrogen, and triplet or quintet for oxygen. Table I gives the A's for both choices. In practical calculations the results are insensitive to which calibration we choose. We therefore did not attempt any averaging of the term values or parameters A.

IV. DIATOMIC MOLECULES

We now discuss the application of this model potential to the calculation of various Rydberg states of the diatomic molecules nitrogen, oxygen, nitric oxide, and carbon monoxide. Table II gives the parameters, A, of the model potential for the carbon, nitrogen, and oxygen cores. Each atomic core also has an effective charge $\delta Z=\frac{1}{2}$ [Eq. (5)]. The Rydberg energy levels are just the eigenvalues of the model Hamiltonian

$$(-\tfrac{1}{2}\nabla^2+V_{\text{mol}})\psi_n=\epsilon_n\psi_n, \tag{15}$$

where V_{mol} is a sum of atomic model potentials and therefore, has the symmetry of the molecular framework. Recall that all adjustable parameters are fixed by calibration to atomic data and that V_{mol} has no additional adjustable parameters. Next we expand the Rydberg molecular orbital, ψ_n, as a linear combination of Gaussian-type orbitals. These orbitals can be placed at arbitrary centers including the atomic centers and the midpoint of the bond. We will see that in other polyatomic systems the Gaussian orbitals can be placed at points completely off the molecular framework. We use only S- and P-like orbitals with radial parts of the form $\exp(-\alpha r^2)$ and $r\exp(-\beta r^2)$, respectively. Table III

TABLE II. Parameters for atomic model potentials.

Atom	A[a]	r_0[a]
C	0.375	2.5
N	0.115	2.5
O	0.045	2.5

[a] In atomic units. See Eq. (5).

lists the exponents α and β which we used for all calculations on diatomic molecules. The basis set includes some very diffuse functions which can adequately describe the high members of various Rydberg series. We have experienced no instability problem with these diffuse functions. More importantly, the use of Guassian functions allows us to extend this method to large polyatomic molecules since the necessary integrals for such calculations are easily evaluated for a Gaussian basis set.

The ground state of N_2, $(X\ ^1\Sigma^+g)$, has the electron configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2$. We consider Rydberg orbitals of the following symmetry $ns\sigma_g$, $np\sigma_u$, $np\pi_u$, $nd\sigma_g$, and $nd\pi_g$. The experimentally observed Rydberg states correspond to an electron in one of these orbitals and one of the following three cores:

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g) \quad X\ ^2\Sigma_g^+,$$
$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2 \quad A\ ^2\Pi_u,$$
$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)(1\pi_u)^4(3\sigma_g)^2 \quad B\ ^2\Sigma_u^+.$$

In our simple model we assume these three cores to be identical and therefore specified by the same atomic model potentials. With the basis functions of Table III we solve Eq. (15) for Rydberg eigenvalues using the Jacobi method for matrices. Table IV gives the results measured in electron volts below any of the three ionization potentials, 15.58, 16.69, and 18.76 eV for the $X\ ^2\Sigma_g^+$, $A\ ^2\Pi_u$, and $B\ ^2\Sigma_u^+$ states of N_2^+, respectively.

The results are encouraging. We can readily identify four Rydberg series in good agreement with the avail-

TABLE III. Gaussian basis set for diatomic calculations.

	Orbital exponents	
	s functions	p functions
ns, $np\sigma$, and $np\pi$ series		
Centers A[a] and B	0.45	0.45
	0.15	0.15
Molecular midpoint	0.05	0.05
	0.0166	0.0166
	0.0055	0.0055
	0.0018	0.0018
	0.0006	0.0006
$nd\sigma$ series		
Centers A[a] and B		0.45
		0.15
		0.05
Centers C[b] and D		0.0166
		0.0055
		0.0018
		0.0006
$nd\pi$ series		
Centers A[a] and B		0.15
		0.05
		0.0166
Centers C[b] and D		0.0055
		0.0018
		0.0006

[a] The atoms are at centers A and B.
[b] Center C is 3 a.u. to the right of B and center D 3 a.u. to the left of A.

TABLE IV. Rydberg levels for N_2.[a]

Rydberg orbital symmetry	Calculated term values[b]	Experimental term values	Fit to Rydberg formula[b]
$3s\sigma_g$	3.80	3.65[c]	3.77[d]
$4s\sigma_g$	1.61		1.62
$5s\sigma_g$	0.88		0.89
$6s\sigma_g$	0.53		0.57
$4p\sigma_u$	2.60	2.80[e]; 2.11[f]	2.60[g]
$5p\sigma_u$	1.23	1.26	1.26
$6p\sigma_u$	0.72	0.73	0.74
$7p\sigma_u$	0.45	0.49	0.49
$3p\pi_u$	2.63	2.21[h]	2.63[i]
$4p\pi_u$	1.26		1.27
$5p\pi_u$	0.77		0.75
$6p\pi_u$	0.47		0.49
$4d\sigma_g$	2.70	2.71[j]	2.69[k]
$5d\sigma_g$	1.35		1.29
$6d\sigma_g$	0.79		0.75
$7d\sigma_g$	0.40		0.49
$4d\pi_g$	2.52[l]		

[a] Internuclear distance of 2.113 a.u.
[b] All term values in electron volts.
[c] Average of term values for states $^1\Sigma_g^+$ and $^3\Sigma_g^+$ [(core) $(2\sigma_u)^2\times(1\pi_u)^4(3\sigma_g)(ns\sigma_g)$] at 3.4 and 3.71 eV, respectively, $o\ ^1\Pi_u$ [(core) $(2\sigma_u)^2\times(1\pi_u)^3(3\sigma_g)^2(ns\sigma_g)$] at 3.59 eV, $^1\Sigma_u^+$ [(core) $(2\sigma_u)(1\pi_u)^4(3\sigma_g)^2(ns\sigma_g)$] at 3.89 eV.
[d] With a term defect $\delta=1.1$.
[e] Average of term values for states $p'\ ^1\Sigma_u^+$ and $D\ ^3\Sigma_u^+$ [(core) $(2\sigma_u)^2\times(1\pi_u)^4(3\sigma_g)(4p\pi_u)$] at 2.65 and 2.95 eV, respectively. For experimental values listed in this column see Ref. 8.
[f] $y\ ^1\Pi_g$ [(core) $(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2(4p\sigma_u)$].
[g] With a term defect $\delta=1.71$.
[h] Average of term values for states $^1\Pi_u$ and $^3\Pi_u$ [(core) $(2\sigma_u)^2(1\pi_u)^4\times(3\sigma_g)(3p\pi_u)$] at 2.11 and 2.40 eV, respectively, $z\ ^1\Delta_g$ and $x\ ^1\Sigma_g^-$ [(core) $\times(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2(3p\pi_u)$] at 2.02 and 2.29 eV, respectively.
[i] With a term defect $\delta=0.73$.
[j] $h\ ^1w_u^+$ [(core) $(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2(4d\sigma_g)$] at 2.71 eV.
[k] With a term defect $\delta=1.75$.
[l] No state with this configuration has been definitely identified. See text for discussion.

able experimental data. These are the ns series with a term defect $\delta=1.1$, $np\sigma$ series with $\delta=1.71$, $np\pi$ series with $\delta=0.73$, and the $nd\sigma$ series with $\delta=1.75$. With the simple model potential and Gaussian functions we obtain four members of each series with a few minutes of computer time. The $3s\sigma_g$ is the only member of the ns series well identified experimentally. Our predicted term value of 3.80 eV agrees well with the experimental values of 3.4 and 3.71 eV for the $^1\Sigma_g^+$ and $^3\Sigma_g^+$ states arising from a $3\sigma_g\rightarrow ns\sigma_g$ transition, and the 3.59 and 3.89 eV for the $o\,^1\Pi_u$ and $^1\Sigma_u^+$ states arising from $1\pi_u\rightarrow ns\sigma_g$ and $2\sigma_u\rightarrow ns\sigma_g$ transitions, respectively. For the $np\sigma$ series the $4p\sigma_u$ to $7p\sigma_u$ members have been identified experimentally. The calculated term values for this series are in good agreement with these results. The calculated term value for the lowest member of the $nd\sigma$ series is 2.70 eV. Mulliken has suggested that the $h\,^1\Sigma_u^+$ state at 13.98 eV above the ground state of N_2 may be a member of the $nd\sigma$ series with configuration (core) $(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2(nd\sigma_g)$. This state then has a term value of 2.71 eV in very good agreement with our predicted term value of 2.70 for the $4d\sigma_g$ Rydberg state. Finally, no member of the $nd\pi$ series has been definitely identified. The calculated term value for the first member of this series, i.e., $4d\pi_g$ orbital, is 2.52 eV. This does rule out the possibility that the state observed at 13.184 eV with a $A\,^2\Pi_u$ core $[(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2]$ could be a $^1\Sigma_u^+$ state since the Rydberg orbital would necessarily be $\pi_g(4d\pi_g)$ and consequently should lie at about 14.2 eV.

Finally the calculated term values in Table IV agree very well with those obtained by Lefebvre-Brion and Moser[9] by direct Hartree–Fock calculations. For example, some term values obtained from their Tables III–V are 3.68 and 1.68 eV for the $3s\sigma_g$ and $4s\sigma_g$ members of the ns series; 2.48, 1.18, and 0.68 eV for the $4p\sigma_u$, $5p\sigma_u$, and $6p\sigma_u$ members of the $np\sigma$ series, 2.48, 1.08, and 0.58 for the $3p\pi_u$, $4p\pi_u$, and $5p\pi_u$ members of the $np\pi$ series. The term values for the higher members of the Rydberg series can be obtained much more economically by our procedure than by direct Hartree–Fock calculations.

Next we consider the Rydberg spectrum of O_2. The ground state of $O_2(^3\Sigma_g^-)$ has the electron configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2$. Again we calculate term values for states with Rydberg orbitals of the following symmetries: $ns\sigma_g$, $np\sigma_u$, $np\pi_u$, $nd\sigma_g$, and $nd\pi_g$. The possible configurations and states of the ions to which these series converge are [10,11]

(core) $(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)$ $X\,^2\Pi_g$,

(core) $(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^3(1\pi_g)^2$ $a\,^4\Pi_u$ and $A\,^2\Pi_u$, etc.,

(core) $(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)(1\pi_u)^4(1\pi_g)^2$ $b\,^4\Sigma_g^-$ and $B\,^2\Sigma_g^-$, etc.,

(core) $(2\sigma_g)^2(2\sigma_u)(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2$ $c\,^4\Sigma_u^-$, etc.

TABLE V. Rydberg levels for O_2.[a]

Rydberg orbital symmetry	Calculated term values[b]	Experimental term values[b]	Fit to Rydberg formula[b]
$3s\sigma_g$	3.97	3.71[c]	3.97[d]
$4s\sigma_g$	1.67	1.66[e]	1.67
$5s\sigma_g$	0.90	0.93[f]	0.92
$6s\sigma_g$	0.53	0.59[f]	0.58
[g]$4p\sigma_u$	2.64	2.54[h]	2.64[j]
$5p\sigma_u$	1.25	1.25[i]	1.27
$6p\sigma_u$	0.73	0.74[i]	0.75
$7p\sigma_u$	0.45	0.49[i]	0.49
$4d\pi_g$	1.55	1.49[k]	1.55[l]
$5d\pi_g$	1.02	0.83	0.87
$6d\pi_g$	0.55	0.53	0.56
$3d\sigma_g$	2.82		2.82[m]
$4d\sigma_g$	1.34		1.33
$5d\sigma_g$	0.72		0.77

[a] Internuclear distance of 2.282 a.u.

[b] All term values in electron volts.

[c] Average of term values for states $^3\Sigma_u^-[(^4\Sigma_u^-$ core) $3s\sigma_g]$ at 3.70 eV, $^5\Pi$ and $^3\Pi$ states at 3.87 and 3.61 eV, respectively, arising from $^4\Pi$ of the O_2^+ ion, $^3\Pi$ and $^1\Pi$ states at 3.84 and 3.51 eV, respectively, arising from $^2\Pi$ of O_2^+.

[d] With a term defect $\delta=1.15$.

[e] Average of term values for states $^3\Sigma_u^-[(^4\Sigma_u^-$ core) $4s\sigma_g]$ at 1.70 eV; $^5\Pi$ and $^3\Pi$ states at 1.65 and 1.49 eV, respectively, arising from $^4\Pi$ of the O_2^+ ion, $^3\Pi$ state at 1.77 eV arising from the $^2\Pi$ of O_2^+.

[f] $^3\Sigma_u^-[(^4\Sigma_u^-$ core) $ns\sigma_g]$ for $n=5$, 6.

[g] The results for the $np\pi_u$ and $sp\sigma_u$ series are almost identical but the $np\pi$ series begins at $n=3$ with $\delta=0.74$. Experimentally, the two series have not been definitely distinguished since in most cases $np\pi_u$ and $np\sigma_u$ both lead to allowed transitions.

[h] Average of term values for states arising from $[(^2\Sigma_g^-$ core) $4p\sigma_u$ or $3p\pi_u]$ at 2.65 eV, $[(^4\Sigma_g^-$ core) $4p\sigma_u$ or $3p\pi_u]$ at 2.87 eV, and $[(X\,^2\Pi_g$ core) $4p\sigma_u$ or $3p\pi_u]$ at 2.48 and 2.16 eV.

[i] Average for states arising from $[(^2\Sigma_g^-$ core) $np\sigma_u$ or $np\pi_u]$ and $[(^4\Sigma_g^-$ core) $np\sigma_u$ or $np\pi_u]$ at 1.27 and 1.22 eV, respectively, for $n=5$, 0.74 and 0.73 eV for $n=6$, 0.49 and 0.48 eV for $n=7$, respectively.

[j] With a term defect $\delta=1.74$.

[k] $^3\Pi_u[(^4\Sigma_u^-$ core) $nd\pi_g]$ states. See Ref. 11 and text for discussion. We assign their state at 3.70 eV to the ns series.

[l] $\delta=1.04$.

[m] $\delta=0.80$.

The ionization potentials of these states are 12.08 eV ($^2\Pi_g$), 16.11 and 16.82 eV ($^4\Pi_u$, $^2\Pi_u$), 18.17 and 20.31 eV ($^4\Sigma_g^-$, $^2\Sigma_g^-$), and 24.56 eV ($^4\Sigma_u^-$). The simple model potentials we use do not distinguish between these various cores. In Table V we therefore list the term values by the symmetry of the Rydberg orbital.

We can identify four Rydberg series in agreement with available experimental data and Leclercq's calculations.[12] These are the ns series with a term defect $\delta=1.15$, $np\sigma$ series with $\delta=1.73$, $np\pi$ series with $\delta=0.74$, and the $nd\pi$ series with $\delta=1.04$. Unlike N_2 the $ns\sigma_g$ series is well identified from $n=3$ to 6. Agreement with experiment is good for the series converging to the $^4\Pi_u$ or $^2\Pi_u$ state of O_2^+.[13] Codling and Madlen[11] report an ns series converging to the $c\,^4\Sigma_u^-$ state of O_2^+ but with term values of 1.70, 0.93, and 0.59 eV. They assign an observed state with a 3.70-eV term value to the $nd\pi$ series. Our results for the ns and $nd\pi$ series clearly show

TABLE VI. Rydberg levels for CO.[a]

Rydberg orbital symmetry	Calculated term values[b]	Experimental term values[b]	Fit to Rydberg formula[b]
$3s\sigma$	3.68	3.23[c]	3.68[f]
$4s\sigma$	1.57	1.64[d]	1.59
$5s\sigma$	0.86	0.80[e]	0.88
$6s\sigma$	0.52	0.51	0.56
$4p\sigma$	2.55	2.61[g]	2.54[i]
$5p\sigma$	1.21	1.19[h]	1.24
$6p\sigma$	0.71	0.70	0.73
$7p\sigma$	0.45	0.46	0.48
$3p\pi$	2.59	2.49[j]	2.59[l]
$4p\pi$	1.26	1.24[k]	1.26
$5p\pi$	0.73	0.73	0.74
$6p\pi$	0.46	0.48	0.49
$4d\pi$	1.58	1.73[m]	1.58[m]
$5d\pi$	1.03	0.95	0.88
$6d\pi$	0.55	0.59	0.56

[a] Internuclear distance of 2.132 a.u.
[b] All term values in electron volts.
[c] $B\ ^1\Sigma^+$ state [$(X\ ^2\Sigma^+$ core) $3s\sigma$]. See Ref. 10.
[d] Σ state [$(X\ ^2\Sigma^+$ core) $4s\sigma$]. This state was previously assigned as the $F\ ^1\Pi$. See text for discussion.
[e] Takamine, Tanaka, and Iwata's Rydberg series converging to the $X\ ^2\Sigma^+$ core. See Ref. 10.
[f] With a term defect $\delta = 1.08$.
[g] $C\ ^1\Sigma^+$ state [$(X\ ^2\Sigma^+$ core) $4p\sigma$].
[h] The diffuse series of Tanaka's β bands. See Refs. 10 and 16. This series converges to the $B\ ^2\Sigma^+$ ion.
[i] With a term defect $\delta = 1.72$.
[j] $^1\Pi$ [$X\ ^2\Sigma^+$ core) $3p\pi$]. This state was previously assigned as $E\ ^1\Sigma^+$ but correctly reassigned as a Π state in Ref. 14. See text.
[k] The sharp series of Tanaka's β bands. See Ref. 16.
[l] With a term defect $\delta = 0.74$.
[m] Our suggested assignment for Ogawa's B–X Rydberg series IV. See Ref. 16 and text for discussion and assignment of the B–X Rydberg series III.
[n] With a term defect $\delta = 1.07$.

that the state with a term value of 3.70 eV belongs to the ns series. In Table V we have not listed the calculated term values for the $np\pi$ series since they are almost identical with the $np\sigma$ series. The agreement with experiment is again good. The $np\sigma$ and $np\pi$ have not been clearly distinguished experimentally since they both lead to dipole-allowed states, $^3\Sigma_u$ and $^3\Pi_u$.

Table VI lists the results of similar calculations for the Rydberg states of CO. The ground state configuration of CO($^1\Sigma^+$) is $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$. We calculate term values for states with Rydberg orbitals of the following symmetries: $ns\sigma$, $np\sigma$, $np\pi$, and $nd\pi$. The three possible cores for these Rydberg series are

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma) \quad X\ ^2\Sigma^+,$$
$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^3(5\sigma)^2 \quad A\ ^2\Pi,$$
$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)(1\pi)^4(5\sigma)^2 \quad B\ ^2\Sigma^+,$$

which lie at 14.01, 16.54, and 19.67 eV above the ground state of CO. As before, the simple molecular model potentials we use do not distinguish between these various cores. We can readily identify three Rydberg series in agreement with experiment. These are the $ns\sigma$ series with $\delta = 1.08$, the $np\sigma$ series with $\delta = 1.73$, and the $np\pi$ series with $\delta = 0.74$. The state with $3s\sigma$ orbital is clearly the $B\ ^1\Sigma^+$ state. Our calculated term value for the second member of the $ns\sigma$ series is 1.57 eV, i.e., at 12.44 eV, confirming that the state at 12.264 eV is not the $F\ ^1\Pi$ state but a Σ state.[14,15] The $5p\sigma$, $6p\sigma$, and $7p\sigma$ members of the $np\sigma$ series and similarly the $np\pi$ series are in good agreement with the diffuse and sharp series, respectively, of Tanaka's β bands.[16] The Π state [$(X\ ^2\Sigma^+$ core) $3p\pi$] with a term value of 2.49 eV was previously identified as the $E\ ^1\Sigma^+$ state. This confirms the reassignment suggested in Ref. 14. In studying the Rydberg series converging to the $B\ ^2\Sigma^+$ state of CO^+ Ogawa observed two new series in addition to the Tanaka's sharp and diffuse series of the β band. These series (III and IV) have not been assigned. In both cases the observed Rydberg bands are due to transitions between an upper $^1\Sigma^+$ or $^1\Pi$ state and the $X\ ^1\Sigma^+$ ground state of CO. Configurations [$(B\ ^2\Sigma^+$ core) $np\pi$] and [$(B\ ^2\Sigma^+$ core) $np\sigma$] have already been assigned to the upper state of Tanaka's sharp and diffuse series. We

TABLE VII. Rydberg levels for NO.[a]

Rydberg orbital symmetry	Calculated term values[b]	Experimental term values[b]	Fit to Rydberg formula[b]
$3s\sigma$	3.88	3.82[c]	3.88[g]
$4s\sigma$	1.64	1.66[d]	1.65
$5s\sigma$	0.89	0.93[e]	0.91
$6s\sigma$	0.53	0.57[f]	0.57
$4p\sigma$	2.62	2.74[h]	2.62[i]
$5p\sigma$	1.24	1.27	1.27
$6p\sigma$	0.72	0.74	0.74
$7p\sigma$	0.45	0.48	0.49
$3p\pi$	2.65	2.78[j]	2.65[k]
$4p\pi$	1.28	1.30	1.28
$5p\pi$	0.74		0.75
$6p\pi$	0.46		0.49
$4d\sigma$	2.75	2.66[l]	2.75[m]
$5d\sigma$	1.31	1.25	1.31
$6d\sigma$	0.70		0.76

[a] Internuclear distance of 2.176 a.u.
[b] All term values in electron volts.
[c] $A\ ^2\Sigma^+$ state [$(^1\Sigma^+$ core) $3s\sigma$].
[d] Average of term values for states $E\ ^2\Sigma^+$[$(^1\Sigma^+$ core) $4s\sigma$] and $^2\Sigma^+$ [$(a\ ^3\Sigma^+$ core) $4s\sigma$] at 1.72 and 1.60 eV, respectively.
[e] Average of term values for states $S\ ^2\Sigma^+$[$(^1\Sigma^+$ core) $5s\sigma$] and $^2\Sigma^+$ [$(a\ ^3\Sigma^+$ core) $5s\sigma$] at 0.95 and 0.90 eV, respectively.
[f] Member of Tanaka's α series. See K. Huber, Helv. Phys. Acta **34**, 929 (1961).
[g] With a term defect $\delta = 1.13$.
[h] Tanaka's β series with configuration $[(1\sigma)^2 \cdots (5\sigma)^2(1\pi)^3(2\pi)np\sigma]^2\Sigma^+$. These are within a few percent of the term values of the γ series.
[i] With a term defect $\delta = 1.72$.
[j] $C\ ^2\Pi$ and $K\ ^2\Pi$ states [$(^1\Sigma^+$ core) $3p\pi$ and $4p\pi$].
[k] With a term defect $\delta = 0.74$.
[l] $D\ ^2\Sigma^+$ and $M\ ^2\Sigma^+$ states [$(^1\Sigma^+$ core) $4d\sigma$ and $5d\sigma$]. See Ref. 18.
[m] With a term defect $\delta = 0.78$.

suggest that the electron configuration of the upper state in series IV is $[(B\,^2\Sigma^+$ core$)\,nd\pi]$, $^1\Pi$. The calculated $5d\pi$ and $6d\pi$ term values agree well with such an assignment but there is a 0.15-eV difference between the calculated and the proposed experimental term value for the $4d\pi$ member. This is probably within the limits of accuracy of our model. For the Rydberg series III[16] with term values 1.47, 0.83, 0.53, and 0.37 eV we propose an electron configuration $[(B\,^2\Sigma^+$ core$)\,ns\sigma]$, $n=4$, 5, 6, and 7. This is in fair agreement with the calculated term values of 1.57, 0.86, and 0.52 eV for the $4s\sigma$, $5s\sigma$, and $6s\sigma$ numbers.[17]

Finally we have calculated term values for possible Rydberg series of the NO molecule. The experimentally observed Rydberg states converge to one of the following ions:

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(1\pi)^4 \qquad {}^1\Sigma^+,$$

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(1\pi)^3(2\pi) \qquad a\,{}^3\Sigma^+,$$

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)(1\pi)^4(2\pi) \qquad {}^1\Pi$$

lying at 9.27, 14.22, and 18.33 eV above the ground state of NO. There is another state of unknown symmetry with the same configuration as the $a\,^3\Sigma^+$ at 16.56 eV. This is the limit of Tanaka's β series. From Table VII the calculated term values of the $ns\sigma$ and $np\sigma$ series with term defects 1.13 and 1.72, respectively, agree very well with experiment. The $C\,^2\Pi$ and $K\,^2\Pi$ states are clearly the first and second members of the $np\pi$ series. The $D\,^2\Sigma^+$ and $M\,^2\Sigma$ are listed as having the united atom forms $[(^2\Sigma^+$ core$)\,4d\sigma$ and $5d\sigma]$ although at the equilibrium distance the separated atom forms $3p\sigma$ and $4p\sigma$ may be more appropriate.[18] The calculated term values are in good agreement with those calculated by direct matrix Hartree–Fock techniques for the Rydberg series converging to the $^1\Sigma^+$ ion.[19]

V. POLYATOMIC MOLECULES

A. Ethylene

The use of these simple model potentials and Gaussian orbitals makes it possible to study the Rydberg series of polyatomic molecules quite easily. First we consider the possible Rydberg states of ethylene. This example illustrates the need for being able to systematically sort out Rydberg states from valence-shell excited states in an SCF calculation of these states. Wilkinson has studied the Rydberg spectra in some detail.[20]

In its ground state the ethylene molecule is planar. With the x axis perpendicular to the plane of the molecule and the z axis along the C–C bond the electronic configuration of the ground state in D_{2h} symmetry is

$$(\Sigma)(1b_{3u})^2=(1a_g)^2(b_{1u})^2(2a_g)^2(2b_{1u})^2 \times(1b_{2u})^2(3a_g)^2(1b_{3g})^2(1b_{3u})^2. \quad (16)$$

TABLE VIII. ns series in ethylene with different model potentials.[a]

"Singlet" C-atom potential	"Triplet" C-atom potential	H-atom model potential included
3.42	3.60	3.35
1.49	1.55	1.48
0.84	0.86	0.83

[a] All results in electron volts. See Sec. V for Discussion.

The $1b_{3u}$ orbital is the π MO. Excitation of an electron from the π MO to the π^* MO gives a $^3B_{1u}$ and $^1B_{1u}$ state. These are the spectroscopic T and V states, respectively. The π^* MO is the $1b_{2g}$ orbital. We consider Rydberg states converging to the $C_2H_4^+$ ion with configuration $(\Sigma)(1b_{3u})$, $^2B_{3u}$, which lies at 10.52 eV above the ground state. For dipole-allowed transitions the Rydberg (upper) state must be B_{3u}, B_{2u}, or B_{1u} with x, y, and z polarization, respectively. In B_{3u} states the Rydberg orbital is an a_g orbital. The a_g orbital becomes an ns orbital in the united atom limit. Similarly, for B_{2u} states the Rydberg orbital is of symmetry b_{1g} and this becomes $nd_{xy}(nd\delta)$ in the UAO limit. The B_{1u} state has a Rydberg orbital of b_{2g} symmetry which becomes nd_{xz} $(nd\pi)$ in the united atom limit. Note that the spectroscopic V state also has $^1B_{1u}$ symmetry. We will also calculate term values for the dipole forbidden states of configuration $(\Sigma)(1\pi)(np_x,\ np_y,$ or $np_z)$.

The model potential for the molecular core is to be the sum of atomic model potentials with no additional adjustable parameters. The model potential of the positive ion core of ethylene would then be approximated by the sum of the model potentials of the two carbon atoms and the four hydrogen atoms in their appropriate valence states. On a physical basis we can expect the term values of Rydberg series for ethylene to depend only very slightly on the contribution of the hydrogen atoms to the molecular model potential. To show this and to assess the dependence of term values on the parameters of the carbon atom model potential we calculated the ns term values for three different model situations. The results are shown in Table VIII. Those in the first column are those obtained using the singlet parameters for the carbon core while those in the second column are obtained using the triplet parameters for the carbon core.[21] In both cases hydrogen atom contributions were neglected. The results in the third column are those of a model which attempts in a very crude fashion to include the effect of the hydrogen atom potential by using a potential of the same form as Eq. (5) but with $A=0.0$ and $\delta Z=0.04$. This value of δZ is consistent with Pauling's ideas on the ionic character of the C–H bond. The carbon singlet parameters were used but with $\delta Z=0.42$. The basis set used in all calculations on ethylene is shown in Table IX. Clearly the term values depend only slightly on any potential

TABLE IX. Gaussian basis set for ethylene calculations.

	Orbital exponents	
	p functions	*s* functions
ns and *npσ* series		
Molecular midpoint	0.05	0.05
	0.0166	0.0166
	0.0055	0.0055
	0.0018	0.0018
	0.0006	0.0006
Centers *A* and *B*[a]	0.45	0.45
	0.15	0.15
ndσ series		
Centers *A* and *B*[b]	0.45	
	0.15	
	0.05	
Centers *C* and *D*[c]	0.0166	
	0.0055	
	0.0018	
	0.0006	
npπ and *ndπ* series		
Centers *A* and *B*[b]	0.15	
	0.05	
	0.0166	
Centers *C* and *D*[c]	0.0055	
	0.0018	
	0.0006	

[a] On the z axis with coordinates 1.265 and −1.265 a.u., respectively.
[b] On the z axis with coordinates 1.265 and −1.265 a.u., respectively.
[c] On the z axis at 4.265 and −4.265 a.u., respectively.

due to the H atoms and on small changes in the parameters of the C atom potential. Hence for all calculations we used the C-atom singlet parameters and did not include any contribution to the core potential from the H atoms.

Table X shows the term values for the various Rydberg series of ethylene. The calculated term values for the *ns* series agree well with Wilkinson's measurements.[20] Typical of *ns* series it shows a term defect of 1. This is his *nR* series.[20] Wilkinson identified three other Rydberg series all involving dipole-allowed upper states. These are the *nR′*, *nR″*, and *nR‴* series. For a dipole-allowed transition the Rydberg orbital must be a_g, b_{1g}, or b_{2g}. The calculated term values for the *ndσ* series, i.e., 2.32 and 1.15 eV, agree very well with those of the *nR′* series, 2.26 and 1.16 eV. We therefore assign Wilkinson's *nR′* series as a *ndσ* series, $n=4, 5, \cdots$, with $\delta=1.58$. This term defect seems reasonable since this series has a $3d\sigma$ ($3a_g$ MO) core ancestor. Wilkinson assigned the state observed at 73011 cm^{-1} (9.05 eV) as the first member of the *nR‴* series. The calculated term values for the *ndπ* (b_{2g} MO) series are 1.52, 0.99, and 0.53 eV. The measured term value of the first member of the *R‴* series is 1.47 eV. We therefore assign Wilkinson's *nR‴* series as a $nd\pi_x$ series, $n=4, 5\cdots$, with $\delta=1$. The first member of this series is hence a B_{1u} state [(Σ core) (π) (b_{2g})] at 9 eV above the ground state. Note that this Rydberg state is of the same symmetry as the *V* state ($^1B_{1u}$) which is due to the $\pi\rightarrow\pi^*$ transition. In the united atom limit the π^* MO becomes $3d\pi_x$. Later in this section we will discuss how the relative location of the *V* state and this Rydberg state changes in going from the experimental to the Hartree–Fock spectrum.

We next assign transitions corresponding to the two *ndδ* series. These *ndδ* orbitals can be $b_{1g}(nd_{xy})$ or $a_g(nd_{x^2-y^2})$ MO's. Wilkinson's *nR″* series has term values of 1.90 and 1.01 eV and a term defect of 0.32. With our present computer programs we cannot calculate the $nd_{x^2-y^2}$ series properly and our calculated term values for the nd_{xy} series are 1.51, 0.99, and 0.54 eV. We therefore assign Wilkinson's *nR″* series as a $nd\delta_{\cos}$, $n=3, 4, \cdots$, series. Wilkinson tentatively assigned states at 8.92, 9.11, and 9.39 eV as members of a possible fifth *nR‴″* series. These give term values of 1.60, 1.41, and 1.13 eV, respectively. We propose that the state at 9.11 eV is probably a vibrational member of

TABLE X. Rydberg levels for C_2H_4.[a]

Rydberg orbital symmetry	Calculated term values	Experimental term values	Fit to Rydberg formula
$3s$ ($4a_g$)[b]	3.42	3.41[c]	3.40[d]
$4s$	1.49	1.62	1.51
$5s$	0.84	0.90	0.85
$6s$	0.51	0.57	0.54
$4d\sigma$ ($5a_g$)	2.32	2.26[e]	2.32[f]
$5d\sigma$	1.15	1.16	1.16
$6d\sigma$	0.60		0.60
$4d\pi$ ($2b_{2g}$)	1.52[g]	1.47[h]	1.51[i]
$5d\pi$	0.99		0.85
$6d\pi$	0.53		0.53
$3p_z$ ($2b_{3u}$)	2.50[j]		2.50[k]
$4p_z$	1.23		1.23
$5p_z$	0.74		0.73
$3d\delta$ (a_g)		1.90[l]	1.89[m]
$4d\delta$		1.01	1.01
$3d\delta$ ($1b_{1g}$)	1.51	1.60[n]	1.50[o]
$4d\delta$	0.99	1.13	0.85
$5d\delta$	0.54		0.53

[a] Carbon–carbon distance 2.53 a.u.
[b] Symmetry designation of the Rydberg orbital. The *ns* series is Wilkinson's *nR* series. See Ref. 20.
[c] Term values for the states $^1B_{3u}$ [(sigma core) π *ns*]. See Ref. 20.
[d] With a term defect $\delta=1$.
[e] Wilkinson's *nR′* series. States are $^1B_{3u}$.
[f] With a term defect $\delta=1.58$.
[g] B_{1u} states.
[h] Wilkinson's *nR‴* series.
[i] With a term defect $\delta=1$.
[j] A_g states [(sigma core) πnp_x]. The np_x, np_y, and np_z series have about the same term values.
[k] $\delta=0.67$.
[l] Wilkinson's *nR″* series.
[m] $\delta=0.32$.
[n] Possibly members of Wilkinson's suggested fifth Rydberg series *nR‴″*.
[o] $\delta\sim0$.

the $4R'''$ series and therefore assign the states with term values 1.60 and 1.13 eV to a nR'''' series, $n=3, 4, \cdots$, with a $nd\delta_{\sin}$ Rydberg orbital. This accounts for the five electric dipole allowed Rydberg series possible in ethylene.

Transitions to states with configuration $[(\Sigma \text{ core})(\pi)(np_x, np_y, \text{ or } np_z)]$ are electric-dipole forbidden. For example, the np_y series would correspond to the electric quadrupole-allowed transition $A_g \rightarrow B_{1g}$. From our calculated term values there should be B_{1g}, B_{2g}, and A_g states at 8.0 eV. The existence of these states may be a part of the explanation of the minimum in the generalized oscillator strength as a function of momentum transfer, $f(K)$, recently observed in the electron impact spectrum of ethylene.[22] It can be shown that Rydberg and valence transitions can be distinguished by the appearance of a minimum in the curve for $f(K)$ for Rydberg transitions while for valence transitions $f(K)$ should decrease monotonically as K increases.[23] This argument is based on the presence or absence of radial nodes in the molecular orbitals involved in the transition. Krauss and Mielczarek[22] have used this characteristic minimum to study the Rydberg character of the excited states corresponding to energy losses of 7.16, 8.0, 8.27, and 9.12 eV. The energy losses at 7.16, 8.17, and 9.12 eV clearly correspond to Rydberg transitions $\pi \rightarrow 3s$, $\pi \rightarrow 4d\sigma$, and $\pi \rightarrow 4s$ with calculated term values 3.4, 2.3, and 1.5 eV, respectively (Table X). In agreement with Miller's theoretical curves[23] minima are observed in $f(K)$ for these three energy losses.[22] To study the orbital character of the V state they chose an energy loss of 8 eV due to the Rydberg peaks lying on top of the $N \rightarrow V$ absorption. The $f(K)$ curve for this energy loss shows a minimum. This is surprising since the V state, with its strong oscillator strength, is usually identified with a valence transition and, like its UAO limit $2p_x \rightarrow 3d\pi$, involves orbitals with no radial nodes. One explanation is that the Rydberg contribution at an energy loss of 8.0 eV is due to dipole-forbidden Rydberg transitions that become allowed as the molecule becomes nonplanar.[22] Our calculations support this explanation since they show three Rydberg states, $\pi \rightarrow 3p_x$, $3p_y$, and $3p_z$, at about 8 eV,[24] all of which become allowed as the molecule is distorted from the planar geometry. The energy of these Rydberg states will change very little as the CH_2 groups twist relative to each other and hence should still be at around 8 eV. The other explanation, namely that there is configurational mixing of considerable Rydberg character with the valence state is still a possibility.[22]

We predict B_{1u} Rydberg states $[(\text{sigma core})(\pi)(nd\pi_x)]$ with term values of 1.52, 0.99, and 0.53 eV. These states are of the same symmetry as the V state. Experimentally the first member should therefore be at 9 eV. However direct SCF calculations on the C_2H_4 ground state and the $C_2H_4^+$ ion give an SCF ionization potential of 9.03 eV.[4] Therefore in the Hartree–Fock approximation we can expect these B_{1u} Rydberg states to be at 7.51, 8.04, and 8.50 eV. Direct SCF calculations with a large basis flexible enough to describe both the valence (π, π^*) state and the Rydberg states $(\pi, nd\pi_x)$ give states at 7.43, 8.13, and 8.64 eV.[4,25] Surprisingly no valencelike (π, π^*) state emerges from these calculations. All the states are clearly very diffuse, e.g., the state at 7.43 eV has a π^* (or $nd\pi_x$) orbital with the matrix element[26] $\langle \pi^* \mid x^2 \mid \pi^* \rangle = 42$ (a.u.)^2. It becomes obvious that only Rydberg states emerge from the SCF approximation and that in this same approximation, the valencelike state probably lies above the energy of the positive ion, i.e., 9.03 eV above the ground state.[4]

B. Benzene

As a final example we shall calculate term values for various Rydberg series of benzene. The model potential of the positive ion core is again approximated by the sum of the model potentials of the six carbon atoms. For the atomic model potential we choose the parameters calibrated to the singlet Rydberg spectrum of the carbon atom (Table I) and $\delta Z = 1/6$. Based on test calculations for ethylene we neglect the contribution of the hydrogen atoms to the molecular potential. The basis set of Gaussian orbitals is shown in Table XI.

With the molecule in the x–y plane the electron configuration of the ground state ($^1A_{1g}$) in D_{6h} symmetry is

$$\mid A_{1g}\rangle = \{\text{core}\}(2e_{2g})^4(3a_{1g})^2(2b_{1u})^2(1b_{2u})^2 \times (3e_{1u})^4(3e_{2g})^4(1a_{2u})^2(1e_{1g})^4, \quad (17)$$

with {core} denoting the core orbitals $(1a_{1g})^2(1e_{1u})^4 \times (1e_{2g})^4(1b_{1u})^2(2a_{1g})^2(2e_{1u})^4$. Wilkinson[27] has observed four Rydberg series in the absorption spectrum of benzene converging to the ionization potential of 9.25 eV. These series thus all correspond to excitation out of the $1e_{1g}$ orbital. The transitions of the nR and nR' series are strong and are clearly dipole allowed. The upper states must be either $^1E_{1u}$ (xy polarized) or $^1A_{2u}$ (z polarized) corresponding to transitions $1e_{1g} \rightarrow npa_{2u}$ and $1e_{1g} \rightarrow npe_{1u}$, respectively.[28] It has usually been assumed that the upper states of the nR series are $^1A_{2u}$ and the nR series assigned as $1e_{1g} \rightarrow npe_{1u}$. The nR' series must then be $1e_{1g} \rightarrow npa_{2u}$ ($^1E_{1u}$ upger states). Our calculated term values suggest the reverse assignment, namely that the nR series is $1e_{1g} \rightarrow npa_{2u}$ ($^1E_{1u}$ states) and the nR' series $1e_{1g} \rightarrow npe_{1u}$ ($^1A_{2u}$ states). The calculated quantum defects (Table XII) are 0.49 and 0.35 for the npa_{2u} and npe_{1u} series, respectively, compared to Wilkinson's term defects of 0.46 and 0.16 for the observed nR and nR' series. We therefore assign Wilkinson's nR and nR' series to $1e_{1g} \rightarrow npa_{2u}$ and $1e_{1g} \rightarrow npe_{1u}$ transitions, respectively. Note that this assignment puts a $^1E_{1u}$ Rydberg state on top of the $N \rightarrow V$ absorption. The V state is definitely $^1E_{1u}(1e_{1g} \rightarrow 1e_{2u})$. We believe that these two states, although of the same symmetry, are so different that very little mixing occurs.

Wilkinson's nR'' and nR''' series are weak and prob-

TABLE XI. Basis set for benzene calculations.

	Orbital exponent		Symmetry of basis function
$ns a_{1g}$ series			
$(-5.272, 0.0, 0.0)$,[a] $[C_6]$[b]	0.45		s
	0.15		s
$(0.0, 0.0, 0.0)$, $[E]$	0.055	0.0018	s
	0.0166	0.0006	s
	0.0055	0.0002	s
$np a_{2u}$ series			
$(-6.0, 0.0, 0.0)$, $[C_6]$	same as ns series		z
$(0.0, 0.0, 0.0)$, $[E]$	same as ns series		z
$np e_{1u}$ series			
$(-4.0, 0.0, 0.0)$, $[C_2]$	same as ns series		y
$(0.0, 0.0, 0.0)$, $[E]$	same as ns series		y
$nd a_{1g}$ series			
$(0.0, 0.0, 1.0)$, $[\sigma_h]$	0.45	0.05	z
	0.15		
$(0.0, 0.0, 4.0)$, $[\sigma_h]$	0.0166	0.0018	z
	0.0055	0.0006	z
$nd e_{1g}$ series			
$(-2.636, 0.0, 0.0)$, $[C_2]$	0.15	0.0166	z
	0.05		
$(-6.0, 0.0, 0.0)$, $[C_2]$	0.0055	0.0006	z
	0.0018	0.0002	
$nd e_{2g}$ series	same as $nd e_{1g}$ series		

[a] (x, y, z) coordinates locating the basis function.
[b] Symmetry operation in D_{6h} locating points with identical basis function.

ably correspond to forbidden transitions which have gained their strength by borrowing intensity from allowed transitions. From the calculated term values (Table XII) the transitions in these series are $1e_{1g} \rightarrow nd$. We can also reasonably assign the R'' and R''' series as $1e_{1g} \rightarrow nde_{1g}$ and nde_{2g}, respectively. These series have term defects of 0.04 and 0.02.

These four series are the only Rydberg transitions studied experimentally by means of ultraviolet absorption. Lassettre[29] has studied the electron impact energy loss spectrum of benzene at high incident electron energy and small scattering angle. Under these conditions only allowed processes are observed. The excitation curve shows one very strong and broad peak at 7.0 eV, strong peaks at 9.4, 11.0, and 12.2 eV, smaller peaks at 10.4 and 13.0 eV, and a very small peak at 12.6 eV. Jonsson and Lindholm[30] have used this spectrum, ultraviolet absorption data, and the results of photoelectron spectroscopy to try to determine the orbital energy levels in ground state benzene. They assign orbital levels to the peaks in the photoelectron spectrum and, from estimated or experimental term values, deduce the resulting excitation curve which is then compared to the experimental curve. Although our assignments of certain peaks in Lassettre's spectrum disagree with theirs,[30] we predict the same orbital energy level scheme. The energies of the $1e_{1g}(\pi)$, $3e_{2g}$, and $1a_{2u}(\pi)$ orbitals are 9.3, 11.4, and 12.1 eV, respectively. The $3e_{1u}$ orbital has an energy of 13.8 eV. However, from our calculated term values, we assign the peaks at 7.0 and 8.2 eV as $1e_{1g} \rightarrow 3pa_{2u}$ and $4pa_{2u}$ transitions, respectively, and those at 7.4 and 8.4 eV as $1e_{1g} \rightarrow 3pe_{1u}$ and $4pe_{1u}$. Our results confirm the assignment of the peak at 11.4 eV in the photoelectron spectrum as the $3e_{2g}$ level since this leads to Rydberg transitions $3e_{2g} \rightarrow 3pe_{1u}$ and $4pe_{1u}$ and $4pe_{1u}$ at 9.4 and 10.4 eV, respectively, in good agreement with Lassettre's peaks at 9.3 and 10.4 eV. We predict a $1a_{2u}(\pi) \rightarrow 3da_{1g}$ transition at 10.1 eV correlating very well with Lassettrre's peak at 10 eV. We would also assign the $3e_{1u} \rightarrow 3sa_{1g}$ and $3e_{1u} \rightarrow 3de_{1g}$ or $3de_{2g}$ transitions, calculated at 11.3 and 12.4 eV, to the strong peaks at 11.0 and 12.2 eV, respectively, in the energy loss spectrum. The small unassigned peak at 12.6 eV is very probably the $3e_{1u} \rightarrow 4sa_{1g}$ predicted at 12.6 eV. Finally the peak at 12.9 eV could also be the $3e_{1u} \rightarrow 4d$ transition.[31] The

TABLE XII. Rydberg levels for benzene.[a]

Rydberg orbital	Calculated term values	Experimental term values[b]	Fit to Rydberg formula
$3sa_{1g}$	2.52		2.53[c]
$4sa_{1g}$	1.21		1.23
$5sa_{1g}$	0.71		0.73
$6sa_{1g}$	0.47		0.48
$3pa_{2u}$	2.16	2.32[d]	2.16[e]
$4pa_{2u}$	1.09	1.10	1.10
$5pa_{2u}$	0.66	0.66	0.67
$6pa_{2u}$	0.44	0.44	0.45
$3pe_{1u}$	2.03	1.84[f]	1.94[g]
$4pe_{1u}$	1.02	0.88	1.02
$5pe_{1u}$	0.62	0.56	0.63
$6pe_{1u}$	0.42	0.39	0.43
$3da_{1g}$	2.01		2.01[h]
$4da_{1g}$	1.01		1.02
$3de_{1g}$	1.40	1.63[i]	1.55[j]
$4de_{1g}$	0.87	0.87	0.87
$5de_{1g}$	0.60	0.56	0.56
$3de_{2g}$	1.38	1.26[k]	1.53[l]
$4de_{2g}$	0.86	0.86	0.86
$5de_{2g}$	0.58	0.55	0.55

[a] A regular hexagon with C–C distance 2.64 a.u.
[b] The electron impact spectrum shows peaks which probably correspond to nsa_{1g} and nda_{1g}. See text for these assignments.
[c] With a term defect $\delta = 0.68$.
[d] Wilkinson's nR series leading to the $^2E_{1g}$ state of $C_6H_6^+$ ion at 9.25 eV. See Ref. 27.
[e] $\delta = 0.49$.
[f] nR' series of Ref. 27. These are $^1A_{2u}$ states.
[g] $\delta = 0.35$.
[h] $\delta = 0.40$.
[i] Wilkinson's nR'' series. This is our assignment.
[j] $\delta = 0.04$.
[k] Wilkinson's nR''' series—our assignment.
[l] Quantum defect $\delta = 0.02$.

calculated term values put the $3e_{1u}\rightarrow 4d$ transition at 12.9 eV and the proposed $1b_{2u}\rightarrow 3de_{2g}$ assignment at 13.1 eV.

We anticipate that calculated term values will be very useful in the interpretation of electron impact spectra of large polyatomic molecules and consequently the assignment of orbital energies to the peaks of the corresponding photoelectron spectrum.

VI. CONCLUSIONS

The main purpose of this work has been to develop and use simple model potentials to calculate the Rydberg series of diatomic and large polyatomic molecules. These model potentials are chosen to reproduce the main features of the exact pseudopotential, i.e., to replace orthogonality constraints in the eigenvalue equation for outer orbitals by adding a nonlocal potential to the single-particle Hamiltonian. To develop a practical scheme for large molecules we represented the effective potential of the molecular core by a sum of model potentials of the constituent atoms.[2] The atomic potentials are calibrated to atomic data and hence the molecular potential contains no further parameters. With Gaussian-type functions to describe the Rydberg orbital the calculations are simple and straightforward requiring little computer time.

The results are very encouraging. The calculated term values agree with the measured values to within 5%–10% in all cases. The s, p, and d series emerge very distinctly not only for the diatomic molecules but also for ethylene and benzene. For the diatomic molecules we have proposed assignments for some series, e.g., the $nd\sigma$ series in N_2 and the $nd\pi$ in CO. In ethylene we have proposed quantitative assignments for all the Rydberg series observed by Wilkinson.[3] The agreement between calculated and measured term values is again 5%–10%. These results have been useful in discussing the results of Hartree–Fock calculations on the excited states of ethylene. They also suggest a partial explanation of the behavior of the generalized oscillator strength as a function of momentum transfer at an energy loss of 8.0 eV in the electron impact spectrum of ethylene.[22] These applications illustrate some of the uses we anticipate for the results of these model calculations.

For benzene our calculated term values indicate that Wilkinson's nR series[27] is due to $1e_{1g}\rightarrow npa_{2u}$. The calculated quantum defect is 0.49 compared to experimental value of 0.46. This means that there is Rydberg state of the same symmetry as the V state lying on top of the $N\rightarrow V$ absorption. One can argue that there should be very little mixing of these states. We also quantitatively assign the three other Rydberg series observed by Wilkinson as $1e_{1g}\rightarrow npe_{1u}$, nde_{1g}, and nde_{2g}. A useful application of the calculated term values is in assigning orbital energies to the peaks in the photoelectron spectrum. With the photoelectron spectrum and calculated terms we can propose an excitation curve, e.g., for electron impact, which can be compared with the experimental curve.[30] In this way we have confirmed Jonsson and Lindholm's result that between the $1e_{1g}$ (9.3 eV) and $1a_{2u}$ (12.1 eV) π levels there is a $\sigma(3e_{2g})$ level at 11.4 eV).

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